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The Solubility of $Pd(NH_3)_2Cl_2$ in Electrolyte Solutions[1]

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Solubilities have been determined at 25° for *trans*-$Pd(NH_3)_2Cl_2$ in solutions of NH_4NO_3, NH_4Cl, and NaCl, in which media base hydrolysis is repressed. The data are interpreted in terms of the heterogeneous equilibrium involving the uncharged solute molecule and the homogeneous equilibrium for the first step of aquation. The concentration of neutral solute in the saturated solution is given as 9.5×10^{-4} M and the aquation equilibrium constant as 3.9×10^{-3}.

The rates and equilibria of aquation (acid hydrolysis) of a number of complexes of Pt(II) containing only Cl^-, H_2O, and NH_3 as ligands have been investigated by Martin and his coworkers.[2] The equilibrium constants range over a factor of nearly 1000, whereas the rate constants for the forward step vary by a factor of less than five,[3] indicating that nearly the entire kinetic effect is to be found in the reverse reaction. Banerjea and Tripathi[4] have suggested that the mechanism of the substitution reactions of Pd(II) differs from that for Pt(II); and this difference is such that it may be expected that, considering the aquation of a series of complexes with various ligands, the effect on the trend in reaction rate within the series caused by replacing Pt by Pd will differ for the forward and the reverse reactions. In such case, the aquation equilibrium constants will vary through the series in qualitatively different ways for the complexes of the two metals.

One example may be seen from the following equilibrium constants for aquation[2,5]: $PtCl_4^{-2}$, 30×10^{-3}; $PtCl_3(H_2O)^-$, 1.0×10^{-3}; $PdCl_4^{-2}$, 3×10^{-3}; $PdCl_3(H_2O)^-$, 4×10^{-3}. An even more profound difference seems to be shown by the report by Banerjea and Tripathi[4] that the aquation of *trans*-$Pd(NH_3)_2Cl_2$ proceeds to completion, while[2] for the *trans*-Pt complex $K = 8 \times 10^{-5}$ and for the *cis*-Pt, K' (at ionic strength 0.3) $= 3.3 \times 10^{-3}$. On the other hand, the interpretation of Banerjea and Tripathi in this connection is based on the assumption that the observed conductivity of the solution is due to the aquation process, whereas it had been recognized earlier[6] that $Pd(NH_3)_2Cl_2$ undergoes a decomposition when placed in contact with water. It therefore seems likely that it was this latter process, rather than aquation, which was observed by Banerjea and Tripathi.

The lack of consistency in the nineteenth century data[7] on the solubility of $Pd(NH_3)_2Cl_2$ also can be attributed to this decomposition. It is the purpose of the present study to determine the solubility under conditions in which the decomposition is prevented and to utilize these data to investigate the aquation equilibria.

The Nature of the Decomposition Process.—Qualitative evidence was obtained for the decomposition by the very noticeable darkening of the solid when put into contact with water, with the formation of a brownish colloidal substance. In solutions unsaturated with respect to $Pd(NH_3)_2Cl_2$ a reddish brown sol formed, and this ultimately coagulated into a brown gel. The presence of the colloidal material rendered phase separation very difficult and led invariably to erratic results in attempts to measure solubility. In the unsaturated solution, decomposition was substantially complete, whereas in the more concentrated systems it was always possible to recover some yellow crystals of starting material, even after prolonged boiling.

It was observed, however, that in the presence

(1) This research was supported in part by the Office of Naval Research.

(2) (a) D. S. Martin, Jr., and R. J. Adams, in S. Kirschner, ed., "Advances in the Chemistry of the Coordination Compounds," The Macmillan Company, New York, N. Y., 1961, p. 579 (includes earlier references); (b) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **81**, 10 (1959); (c) C. I. Sanders and D. S. Martin, Jr., *ibid.*, **83**, 807 (1961); (d) J. W. Reishus and D. S. Martin, Jr., *ibid.*, **83**, 2457 (1961).

(3) For further discussion of this point see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 152ff.

(4) D. Banerjea and K. K. Tripathi, *J. Inorg. Nucl. Chem.*, **7**, 78 (1954).

(5) H. A. Droll, B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, **61**, 1000 (1957).

(6) (a) H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlaw, *J. Chem. Soc.*, 1895 (1932); (b) A. A. Grinberg, V. M. Shulman, and S. I. Khorunzhenkov, *Izv. Inst. Izucheniyu Platiny*, **12**, 119 (1935).

(7) See, *e.g.*, H. Müller, *Liebigs Ann.*, **86**, 341 (1853).

of a sufficient concentration of NH_4^+, Cl^-, or H^+ the darkening did not take place. The highest electrolyte concentrations at which decomposition was observed to occur were: NH_4Cl, 0.0010 *M*; NaCl, 0.015 *M*; NH_4NO_3, 0.005 *M*; HCl, HNO_3, $HClO_4$, less than 0.005 *M*. The color of either partly or completely decomposed $Pd(NH_3)_2Cl_2$ was restored by the addition of NH_4Cl or $HClO_4$. Aqueous $NaNO_3$ had no effect in preventing decomposition and NaOH at millimolar concentrations promoted it.

The following experiment served to identify the ultimate products of decomposition: In 500 cc. of H_2O was placed 0.587 mmole of $Pd(NH_3)_2Cl_2$ (less than saturation) and the mixture was heated at 100° for 4 hr. until coagulation of the precipitate was complete. The solid, after having been dried at 105° for 24 hr., weighed 52.0 mg.; after standing in the air, the mass increased to 54.3 mg. These data are consistent with the formula $PdO \cdot xH_2O$, with x ranging from 0.6 to 1.[8] A portion of the solid was dissolved in 6 *M* HNO_3 and roughly analyzed for Cl, *via* AgCl; Cl found: 4%, corresponding to $^1/_7$ Cl atom per Pd atom.

The colorless filtrate contained at most a trace of Pd, and no excess H^+ or NH_3. NH_4^+ and Cl^- were identified qualitatively; a $^1/_{10}$ aliquot, on evaporation, yielded 4.6 mg. of residue, corresponding to 2.2 moles of NH_4Cl per mole of original $Pd(NH_3)_2Cl_2$.

These observations suggest that the decomposition of the compound results from base hydrolysis in which formation of the hydroxo complex is followed by olation and elimination of NH_3. The prevention of this hydrolysis by H^+ or Cl^- thus is due to interference with the first step. The effect of NH_4^+ in preventing the reaction, however, is too large to be explained on the basis of its acidity. From this fact, and from the observation that in none of the experiments (save only those in which H^+ or OH^- was added) did the pH of the solution differ appreciably from that of the distilled water used (*ca.* 6), it is apparent that approximately one NH_4^+, resulting from NH_3 elimination, accompanies each Cl^- formed in the initial step of the base hydrolysis. (On the other hand, it cannot be asserted whether the hydrolysis proceeds as far as hydrous PdO in the systems saturated with respect to the complex.)

(8) See O. Glemser and G. Peuschel, *Z. anorg. allgem. Chem.*, **281**, 44 (1955).

Experimental

For each determination, the sample of $Pd(NH_3)_2Cl_2$ was agitated in contact with the appropriate salt solution in a constant-temperature bath maintained at 25.00°. Aliquot samples were removed from time to time until the analysis of an initially unsaturated system agreed with that of an initially supersaturated system (prepared by previously warming to *ca.* 40°, at which temperature both solubility and rate of solution are much greater than at 25°). Twenty-four to thirty-six hours was required for equilibrium.

Analysis was performed on samples pipetted through cotton wool. Pd was determined gravimetrically as the salt of dimethylglyoxime, following substantially the procedure of Treadwell and Hall.[9] It was found that a more crystalline precipitate could be obtained for those samples initially low in salt concentration by the addition of ammonium acetate to about 0.01 *M*.

trans-$Pd(NH_3)_2Cl_2$ was prepared following the procedure given by Cohen and Davidson.[10] A sample which had reached equilibrium with an NH_4NO_3 solution analyzed 51.0% Pd; another, from an NH_4Cl solution, 50.8% Pd. Calcd.: 50.4% Pd. Several of the equilibrated solids were tested for the *cis*-isomer, following the procedure of Grinberg and Shulman,[11] with negative results in each case.

Results

In Table I are given the solubilities[12] of $Pd(NH_3)_2Cl_2$ in solutions of NH_4NO_3, NH_4Cl, and NaCl at 25°. Data for systems in which there was noticeable decomposition have not been included.

TABLE I

SOLUBILITIES OF $Pd(NH_3)_2Cl_2$

Salt concn., *M*	Soly., *M*	Salt
0.00939	0.00300	NH_4NO_3
.03052	.00316	NH_4NO_3
.0939	.00334	NH_4NO_3
.00180	.00227	NH_4Cl
.00199	.00226	NH_4Cl
.00300	.00200	NH_4Cl
.00600	.00165	NH_4Cl
.0100	.00141	NH_4Cl
.0150	.00122	NH_4Cl
.0150	.00129	NH_4Cl
.0300	.00113	NH_4Cl
.0601	.00105	NH_4Cl
.1002	.00102	NH_4Cl
.0377	.00106	NaCl
.0754	.00103	NaCl
.1005	.00100	NaCl

(9) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 140.

(10) A. J. Cohen and N. Davidson, *J. Am. Chem. Soc.*, **73**, 1955 (1951).

(11) A. A. Grinberg and V. M. Shulman, *Dokl. Akad. Nauk SSSR*, 215 (1933).

(12) Throughout this paper concentrations are given in units of moles of indicated solute per liter of solution (*M*). Brackets are used around the formulas to indicate such concentration.

Discussion

The solubility data can be explained by considering the equilibria

$$Pd(NH_3)_2Cl_2(s) = Pd(NH_3)_2Cl_2(aq) \quad (1)$$

$$Pd(NH_3)_2Cl_2(aq) + H_2O = Pd(NH_3)_2Cl(H_2O)^+ + Cl^- \quad (2)$$

of which reaction 2 is the first step of aquation. In the development that follows, the solubility product

$$K_s = [Pd(NH_3)_2Cl(H_2O)^+][Cl^-]K_\gamma$$

where K_γ represents the product of the activity coefficients of the two ions. x is the concentration of neutral $Pd(NH_3)_2Cl_2$ in solution, s is the molar solubility, and c the concentration of chloride ion added.[12] It will be assumed that x is constant in all the saturated solutions and that K_γ can be represented by the Güntelberg approximation.[13]

It then follows that

$$s = x + (K_s/K_\gamma)[Cl^-]^{-1} \quad (3)$$

A first approximation for x was found from a plot based on eq. 3 for large values of c, where $[Cl^-] \cong c$. This value of x then was used to construct Fig. 1, in which s is plotted against $(K\gamma[Cl^-])^{-1}$ for the NH_4Cl and NH_4NO_3 points. The intercept agrees with the first approximation of $x = 9.5 \times 10^{-4}\ M$ and the slope gives $K_s = 3.7 \times 10^{-6}$ (molar units); or the equilibrium constant for reaction 2 $= K_s/x = 3.9 \times 10^{-3}$.

The points for the NaCl solutions, if included in Fig. 1, would show a barely perceptible negative

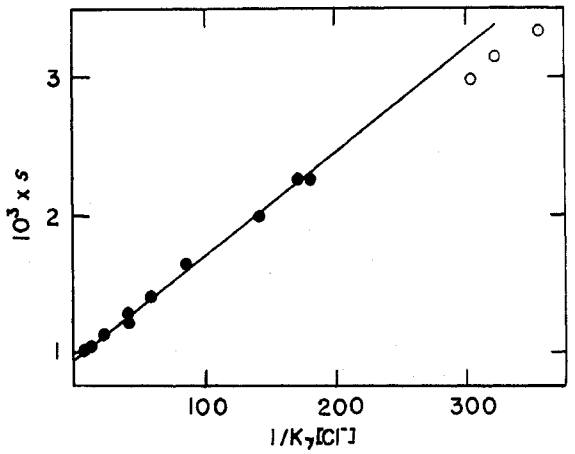

Fig. 1.—Plot of eq. 3: solid circles, NH_4Cl; open circles, NH_4NO_3; concentrations in moles/l.

deviation, due perhaps to a slight extent of base hydrolysis (since the only source of NH_4^+ is from this hydrolysis itself), the chloride from which would tend to lower the solubility. For the NH_4NO_3 solutions, however, there should be sufficient Cl^- from the aquation to prevent decomposition. The observed deviations here may be the result of the approximations made with regard to activity coefficients, both of ions and of the neutral molecule. Such effects would be most pronounced in the NH_4NO_3 solutions, because of the relatively high ionic strength combined with low chloride ion concentration.

A hypothetical solubility of $Pd(NH_3)_2Cl_2$ in water may be obtained from eq. 3 by setting $c = 0$ and estimating K_γ. The result, 0.00297 M, agrees closely with that found by linear interpolation of the NH_4NO_3 data to zero nitrate, 0.00295 M. This agreement, plus the lack of positive deviations from the straight line in Fig. 1 in the region of low chloride, indicates that there is no large tendency for further aquation to $Pd(NH_3)_2(H_2O)_2^{+2}$. On the other hand, a slight extent of this reaction cannot be ruled out: computations performed by selecting K for the second step of aquation as 3×10^{-4} and using K_s as 3.5×10^{-6} (only slightly smaller than found from Fig. 1) showed that the solubility data could be reproduced to within $3 \times 10^{-5}\ M$ for all points in the chloride solutions. On this basis, it is felt that the value given previously for K_s has an uncertainty of perhaps 10%.

If now the equilibrium constant for the aquation of $Pd(NH_3)_2Cl_2$, 3.9×10^{-3}, is compared with those of the several palladium and platinum complexes referred to earlier,[2,5] it is seen that the large variation in K manifested by the Pt compounds does not appear for these particular palladium analogs,[14] consistent with a difference in mechanism of the sort discussed previously. It must be recognized, however, that it is unwarranted to make any more than a general comparison of this kind until isomer analysis data are available for the palladium compounds. Thus, while there is no reason to doubt that all the complexes present in a solution of *trans*-$Pt(NH_3)_2Cl_2$ are in the *trans* configuration, the same cannot be assumed, *a priori*, for the Pd complex. There is no necessary connection between the thermodynamic stability of the *trans* form in the crystalline phase[11] and that in aqueous solution; and the expected electrostatic stabilization of the *trans* form is not always found, as with $Pt(NH_3)Cl_2(H_2O)$[2b] and with

(13) E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

(14) But note the smaller values (ref. 5) for $PdCl_2(H_2O)_2$ and $PdCl(H_2O)_3^+$.